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RELATIONSHIPS OF
STREAM SOLUTES AND HYDROLOGY
DURING SPRING RUNOFF
IN SMALL
SHIELD HEADWATER STREAMS

APRIL 1990



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RELATIONSHIPS OF STREAM SOLUTES AND HYDROLOGY
DURING SPRING RUNOFF
IN SMALL SHIELD HEADWATER STREAMS

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ABSTRACT

The influence of hydrology on changes in $[\text{SiO}_2]$, $[\text{Mg}^{2+}]$ and $[\text{H}^+]$ during snowmelt runoff (1977-1984) was investigated in three small headwater catchments on the Canadian Shield. These catchments differed greatly in their capacity to neutralize acidic deposition (Harp 4, mean stream pH = 6.2; Paint 1, mean stream pH = 5.4; Plastic 1, mean stream pH = 4.4). In Paint 1, none of the three stream solutes studied showed a good relationship with discharge. A centrally located beaver pond was believed to significantly influence stream flow and chemistry. In Harp 4 and Plastic 1, very similar $[\text{SiO}_2]$ -discharge relationships were observed which agreed well with mixing models conceptualizing the stream water as a mixture of soil/groundwater and melt water. Magnesium was only sufficiently greater in soil/groundwater than in the melt water at Harp 4 to produce a similar dilution pattern. Hydrogen was not as highly correlated with discharge in either catchment. Some of the residual variation could be explained by including the change in discharge and a hysteresis effect since $[\text{H}^+]$ was lower on the ascending limb than on the descending limb of the hydrograph.

During periods of high flow the behaviour of $[\text{SiO}_2]$ and particularly $[\text{H}^+]$ differed in Harp 4 and Plastic 1. In Harp 4, discharge remained the most important variable for explaining changes in $[\text{SiO}_2]$ and $[\text{H}^+]$. In Plastic 1, however, antecedent flow and relative change in flow replaced discharge as a significant predictor of $[\text{SiO}_2]$ during high flows. Hydrogen was not well correlated with any hydrologic variables. The lack of a direct relationship between silica and hydrogen behaviour in the two systems suggested that neutralization mechanisms of hydrogen concentrations must differ between Plastic 1 and Harp 4.

A study of individual storm events for Plastic 1 suggested that early melt events had the greatest potential to produce extremely low pH values in the stream. The lowest $[\text{SiO}_2]$ concentrations however, were observed during the major melt runoff period associated with highest flows which occurred later in the melt season. We conclude from the study that hydrology plays a dominant role in influencing the stream chemistry in small Shield headwater catchments during spring runoff.

RÉSUMÉ

L'influence de l'hydrologie sur les changements de $[\text{SiO}_2]$, $[\text{Mg}^{2+}]$ et $[\text{H}^+]$ durant le ruissellement de la fonte des neiges (1977-1984) a été étudiée dans trois petits bassins de sources de cours d'eau du Bouclier canadien. Ces bassins diffèrent beaucoup quant à leur capacité de neutraliser les dépôts acides (Harp 4, pH moyen du cours d'eau = 6.2; Paint 1, pH moyen du cours d'eau = 5.4; Plastic 1, pH moyen du cours d'eau = 4.4). Dans Paint 1, aucun des solutés étudiés indiquait une relation valable avec l'écoulement. Un étang de castor situé au centre du bassin semble avoir eu une influence significative sur le débit et la chimie du cours d'eau. Dans Harp 4 et Plastic 1, des rapports $[\text{SiO}_2]$ -écoulement très similaires ont été observés, correspondant ainsi avec les modèles de mixtion qui conceptualisent l'eau des cours d'eau comme étant un mélange de sol/nappe phréatique et d'eau de fonte des neiges. Dans Harp 4, le magnésium était légèrement plus élevé dans le sol/nappe phréatique que dans l'eau de fonte des neiges, tout juste assez pour produire un modèle similaire de dilution. L'hydrogène n'était pas en corrélation élevée avec l'écoulement dans l'un ou l'autre des bassins. Une partie des variations résiduelles peut s'expliquer en incluant le changement dans l'écoulement et un effet d'hystérèse, étant donné que le $[\text{H}^+]$ était plus bas sur la branche ascendante que sur la branche descendante du graphique hydrologique.

Durant les périodes de débit élevé, le comportement du $[\text{SiO}_2]$, et plus particulièrement celui du $[\text{H}^+]$, sont différents dans Harp 4 et dans Plastic 1. Dans Harp 4, l'écoulement reste la variable la plus importante permettant d'expliquer les changements de $[\text{SiO}_2]$ et de $[\text{H}^+]$. Dans Plastic 1, cependant, le débit antérieur et le changement relatif du débit ont remplacé l'écoulement pour prédire de façon significative le $[\text{SiO}_2]$ durant les débits élevés. L'hydrogène n'accusait pas de corrélation valable avec les variables hydrologiques. L'absence de rapport direct entre le comportement du silice et celui de l'hydrogène dans les deux systèmes suggère que les mécanismes de neutralisation des concentrations d'hydrogène diffèrent entre Plastic 1 et Harp 4.

Une étude des tempêtes individuelles de Plastic 1 suggère que les cas de fontes hâtives avaient le plus grand potentiel pour produire des valeurs de pH extrêmement basses dans le cours d'eau. Cependant, les concentrations de $[\text{SiO}_2]$ les plus basses furent observées durant la période principale de ruissellement, associée aux débits les plus élevés, qui eut lieu plus tard dans la période de fonte des neiges. Cette étude nous permet de conclure que l'hydrologie joue un rôle dominant en influençant la chimie des cours d'eau dans les bassins des petites sources du Bouclier durant le ruissellement printanier.

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1.0 INTRODUCTION

The phenomenon that changes in stream flow are associated with changes in stream chemistry has been observed in catchments of all sizes and characteristics. In general, most stream solutes approach precipitation values as stream flow increases. Various studies have investigated the relationship between stream solutes and hydrology in an attempt to understand more about the hydrological and geochemical processes involved. Initially, concentration-discharge (C-Q) relationships were studied mainly using total dissolved solids (TDS) as a summary measure for salinity. The dilution was empirically described by fitting a best line to the concentration-discharge relationship using hyperbolic (Durum, 1953) and logarithmic equations (Dixon et al. 1970; Pionke and Nicks 1970).

Hall (1970) provided a theoretical framework for the selection of a given equation. Using simple mass balance equations, various solutions for C-Q relationships were developed depending on certain assumptions about the mixing volumes and the storage volume-discharge relationship. Johnson et al. (1969) were the first to apply a mixing model to specific stream solutes such as Na^+ , SiO_2 , Mg^{2+} , SO_4^{2-} , and Cl^- . The optimization of parameters required by some models to fit the long-term records of water chemistry may reveal some information about the hydrology and geochemistry of the system (Hall 1971; Johnson et al. 1969). This approach has often been criticized as an oversimplification of reality since it conceptualizes a catchment as a two component system, in which baseflow (the original volume of groundwater) and direct runoff (input) mix completely.

Several other studies have attempted to represent the influence of flowpaths on stream chemistry by considering flow components derived from hydrograph separation. It was argued by Pionke et al. 1972 that baseflow (delayed flow) and surface flow (quickflow) have different concentrations of total dissolved solids (TDS) such that surface flow acts as a diluent. These authors found that the ratio of surface to baseflow estimated, more precisely than discharge alone, the salinity of ephemeral streams in the Western United States. Walling (1974) further considered a variable TDS concentration for surface flow depending on discharge in order to improve the original concentration-discharge relationship for a small stream in the U.K. Interflow (Hart et al. 1964) as well as antecedent flow as a surrogate of overland flow and/or increased interflow (Ledbetter and Gloyna 1964) have also been considered for improving the C-Q relationship. However, none of these models has been applied to constituents other than total dissolved solids (TDS).

Recent studies have focused on detailed investigations of episodic events. Antecedent basin wetness, and storm magnitude and intensity and their influence on changes in stream chemistry have been examined since they were expected to have an impact on the flowpaths of the event water. Foster (1978) employed a stepwise multiple regression analysis to select the dominating storm characteristics for various stream solutes. Lynch et al. (1986), in a study of changes in pH, alkalinity and total acidity, did not find any of the selected storm parameters to be very significant. However, when used in combination they described the solute response during storm periods very well.

The overall objective of this study was to investigate the relationships between dissolved silica (SiO_2), magnesium (Mg^{2+}), and hydrogen (H^+) and stream hydrology during spring melt runoff in three headwater catchments on the Canadian Shield. The various concentration-discharge relationships were first fitted to selected mixing models based on discharge alone. The use of several flow parameters in predicting stream solute chemistry was then investigated using multiple regression analysis (MRA). Two approaches were considered; a) the entire data base including all baseflow and high flow samples was employed and considered as independent observations; and b) baseflow samples were excluded from the analysis. The comparison of models for the entire flow range and high flow was intended to determine whether the influences of hydrology on the stream solute concentration are similar during these two periods. Finally, changes in stream solute concentration during depicted storm events in Plastic 1 were related to storm characteristics. Dominant storm characteristics were compared to those flow characteristics found to influence the stream solute concentration during periods of high flow.

2.0 DATA BASE

The Harp Lake, Paint Lake and Plastic Lake catchments are located on the Precambrian Shield in the Muskoka-Haliburton area of Central Ontario. They have been monitored since 1976 as part of the Acid Precipitation in Ontario Study APIOS (Dillon et al. 1978; Dillon et al. 1982; Jeffries et al. 1979; Scheider et al. 1979). For the purpose of this project, the streams of three small subcatchments, Harp 4, Paint 1 and Plastic 1, were selected for study.

A summary of catchment characteristics is given in Table 1. It is evident that these catchments differ greatly in their capacity to neutralize acidic deposition (Tables 1 and 2). They are small headwater catchments feeding first and second order streams with peak discharges of less than 30 mm/d during spring runoff and very little or no flow during the late summer period. Their hydrology and stream chemistry is further influenced by wetlands including beaver ponds and/or swamps (Devito et al. 1989).

This study considered only spring runoff data because (1) the highest flows and highest exports of the year are generally observed during this period, (2) Plastic 1 is an ephemeral stream which tends to dry up in some summers, and (3) during the growing season high biological/chemical activity in wetlands (swamps/beaver ponds) combined with very low flows are known to alter chemistry as redox conditions change. Therefore, only observations from January 1 until the 'end of melt runoff' of each year were considered in

Table 1. Description of the study watersheds (in part from Jeffries and Snyder (1983)).

	Plastic 1	Harp 4	Paint 1
Size and location	23.34 ha 45°11' N 78°50' W	119.1 ha 45°23' N 79°08' W	23.15 ha 45°13' N 78°57' W
General morphology	Moderate slopes (< 5%) containing small centrally located swamp covering \approx 9% of the total drainage area	Variable slopes (4-5%) containing small centrally located beaver pond covering \approx 5% of the total drainage area	Steep slopes (10-20%) containing small centrally located beaver pond covering \approx 10% of the total drainage area
Bedrock geology	¹ Ortho-gneiss; mainly igneous granites and meta-sedimentary formations near fault zones	Amphibolite and schist; \approx 15% is underlain by biotite gneiss	Biotite gneiss with minor occurrence of pegmatite dykes
Surficial geology	¹ Shallow discontinuous sandy basal till (< 2m) and exposed bedrock	Unsorted till (1-5m), exposed bedrock and clean well-sorted sand	Unsorted basal till (< 1m) exposed bedrock particularly in stream
Soils and vegetation	² Weakly developed podzolic soils (< 1m) supporting a mostly coniferous forest	² Humo-ferric podzolic soils (1-3m) supporting a mixed hardwood forest	Brunisolic and podzolic soils (> 1m) supporting a mixed hardwood forest

¹ Girard et al. (1985)

² Lozano et al. (1987)

Table 2. Observed minimum, maximum and average concentrations of silica, magnesium and hydrogen (pH) during the spring runoff period in Harp 4 and Paint 1 (1977-1984) and in Plastic 1 (1980-1984). Values for precipitation are given for comparison ([SiO₂] and [Mg] in mg/L Si and mg/L Mg respectively, [H⁺] in µg/L). Data from Dillon (unpub. studies).

	Plastic 1	Paint 1	Harp 4	Precipitation ¹
<u>Silica:</u>				
Range	1.55-5.1	1.75-2.8	1.95-6.1	
Average	2.90	2.38	3.71	< 0.05
Flow weighted average	2.33	2.40	3.00	
<u>Magnesium:</u>				
Range	0.30-0.84	0.5-1.0	0.55-1.38	
Average	0.47	0.75	0.95	0.3-0.4
Flow weighted average	0.46	0.75	0.84	
<u>Hydrogen:</u>				
Range	6.0-63.0	2.0-14.1	0.13-.38	
Average	38.0	4.1	1.03	50.1
Flow weighted average	45.0	5.07	1.71	
<u>pH:</u>				
Range	4.20-5.20	4.85-5.70	5.42-6.90	
Average	4.43	5.41	6.10	4.30
Flow weighted average	4.35	5.32	5.84	

¹ precipitation values from 1987 (Dillon et al. 1988, Dillon, unpub. studies).

this study*. Snowcover records (Environment Canada 1977-1984) from Dorset/Ontario (for Plastic 1) and Dwight/Ontario (for Harp 4) were used to identify the end of melt runoff.

Stream chemical data (silica, magnesium, pH, alkalinity, dissolved organic carbon, and total aluminum) and mean daily discharge records (in L/S) were provided by Dillon and Reid (unpub. studies) for Harp 4 and Paint 1 (1977-1984) and Plastic 1 (1980-1984) (Table 2). Magnesium (Mg^{+}), dissolved silica (SiO_2) and pH (also expressed as $[H^{+}]$) were chosen for analysis for the following reasons.

- 1) the concentrations in stream water and melt water differed greatly in most cases (Table 2);
- 2) the behaviour had been investigated in other field studies for tracing purposes (SiO_2 and Mg^{2+}) or was of environmental concern (hydrogen (pH)).

Runoff from the three basins was gauged at V-notch weirs and continuously recorded using Stevens water level recorders (Scheider et al./ 1983). The daily main discharge is expressed as specific discharge q (in mm/d) throughout this paper for better comparison among watersheds of different size. Water samples were analyzed for pH, usually on the same day using a Radiometer pH meter. Dissolved silica ($SiO_{2\text{ aq}}$) and magnesium (Mg^{2+}) were analyzed within a few weeks of sample collection by colourimetry and atomic adsorption spectroscopy respectively. More detailed outlines of the analytical methods are given in

* Defined as the day of peakflow prior to the final recession of the last melt-dominated storm event and thus prior to any considerable increase in water temperature.

Ontario Ministry of Environment (1983). $[H^+]$ was calculated from pH values and expressed as $\mu g/L$ and $[SiO_2]$ and $[Mg^{2+}]$ are reported in mg/L Si and mg/L Mg respectively.

3.0 CONCENTRATION - DISCHARGE RELATIONSHIPS

Initially, the relationship between various stream solutes (SiO_2 , Mg^{2+}) and discharge alone was investigated for the three APIOS headwater streams during snowmelt runoff. Scatterplots were used to illustrate the general behaviour of the solute to discharge, which could then be statistically compared to proposed mixing models (Johnson et al. 1969; Hall 1970).

3.1 Model Development

The mixing model suggested by Johnson et al. (1969) assumes that stream water is a mixture of two distinct water types, "original" solution (soil/groundwater, volume V_o) and "added" solution (precipitation, volume V_a) with their respective constant concentrations C_o and C_a . The removal of soil water (and its contained chemical load) from a watershed occurs by replacement and/or mixing with in-stream precipitation. A simple mixing model can be derived from a mass balance equation under the following assumptions:

- 1) the volume of water in the system approaches a minimum value V_o when stream discharge approaches 0.
- 2) the volume of water within the system in excess of V_o is directly proportional to stream discharge (q), i.e. $V_a = r \cdot q$ where r is the residence time for water moving through the system.

The concentration of a given solute in the stream can then be expressed as:

$$C = \frac{C_o - C_a}{(1 + \beta * q)} + C_a \quad (1)$$

where C is the solute concentration in the stream, C_o and C_a are the solute concentration in the original (soil/groundwater) and added (melt/rain water) solution and q is the mean daily discharge in mm/d. β is an optimization parameter describing the ratio of residence time of water moving through the system to a minimum volume of water stored in the system during baseflow. Non-linear regression analysis using the Marquardt iterative method (SAS 1985) was performed to determine the best estimates of the parameters β , C_o , and C_a for each solute in the three catchments.

Hall (1970) developed several mixing models on the basis of mass balance equations under the following basic assumptions:

- 1) the storage volume and discharge are proportional and can be expressed in the form of:

$$Q = K * V^n \quad (2)$$

K = constant expressing the residence time

n = constant

- 2) mixing is ideal
- 3) dissolved constituents move in the flow system in the same fashion as the water
- 4) biological uptake and/or evaporation is negligible

The various mixing models developed by Hall (1970) were based on a set of specific assumptions about the mixing volumes and the storage volume-discharge relationships. He derived the same mixing model as Johnson et al. (1969) by postulating a single mixing volume with the restrictions that outflow is equivalent to inflow and that part of the mixing volume remains constant. He further had to assume that the solute concentrations in the inflow and the total load (available amount of solute in the 'system catchment') are constant.

Hall (1970) also suggested a simple log-linear concentration-discharge relationship by specifying that changes in stream solute concentrations are solely a result of changes in the volume (V) of the system:

$$c = a * \log q + b \quad (3)$$

As a result of the numerous and very specific assumptions of this model the actual meaning of the regression coefficient and constant are difficult to conceptualize. The application of Hall's model to this database was not intended to validate the model concept but to provide some control on the uniqueness of the Johnson mixing model (i.e. the appropriateness of a model that required an additional optimization parameter).

The two mixing models were applied to both the original solute concentrations and to concentration which had been normalized to the average concentration of each spring season to test for possible year to year variation in water chemistry.

3.2 Results and Discussion

Silica and Magnesium

A very similar and distinct hyperbolic relationship between Si and discharge was found in Harp 4 and Plastic 1 (Fig. 1-2), suggesting that in these catchments dilution of baseflow by event water is the dominant process influencing the behaviour of silica. Similar decreases in silica with increases in flow have been documented by several authors (Johnson et al. 1969; Kennedy et al. 1986; Lewis and Grant 1979; Foster 1978; Hunt and Foster 1985; Hooper 1986). Keller (1970), however, observed no relationship between silica and discharge when studying small headwater streams in the Swiss Alps. Similarly, Paint 1 silica did not exhibit any relationship with discharge (Fig. 3). A possible reason for this may be the centrally located beaver pond which covers approximately 10% of the area and which may exert a strong influence on the hydrology and stream chemistry of this small basin. The pond has a volume of ca 52 600 m³ which is more than 20 times the typical daily peak run off volume (2600 m³/d). Considerable mixing and/or storage of melt runoff may occur in this pond even during periods of high flow. If this is the case, it is unreasonable to expect a systematic relationship between silica and discharge.

In all of the above mentioned studies observed dilution trends in magnesium were similar to those of silica. In our study, however, decreasing magnesium concentrations with increasing discharge was seen only in Harp 4. Furthermore, silica was highly correlated to magnesium in this catchment indicating that similar processes influence the behaviour of the two solutes in this basin (Fig. 4). Much of the scatter in the relationship between

magnesium and discharge can be removed ($\approx 15\%$) by normalizing measured $[\text{Mg}^{2+}]$ to the average spring concentration. This indicates a considerable variation in magnesium from year to year which is due to factors other than discharge (Table 3). These factors may include:

- 1) very slow weathering processes, thus strengthening the influence of premelt $[\text{Mg}^{2+}]$ in the soil and groundwater;
- 2) a strong influence of seasonal factors such as temperature on weathering processes;
- 3) a potential bias in magnesium and analysis introduced in some years due to changes in analytical procedures or problems of comparability between sample runs.

In Paint 1 and particularly in Plastic 1, a dilution pattern in stream $[\text{Mg}^{2+}]$ was not observed (Figs. 2 and 3 and Table 3) probably due to insufficient difference between baseflow magnesium values and precipitation values.

In Plastic 1 and Harp 4, the two mixing models (Johnson et al. 1969 and Hall 1970) explained the behaviour of silica and magnesium much better than discharge alone suggesting that a linear concentration-discharge relationship would not be an adequate description (Table 3). The very good fit of the mixing models in describing the silica behaviour supports the hypothesis that $[\text{SiO}_2]$ in the stream, while influenced primarily by dilution as mentioned previously, is also the result of the mixing of two components which differ in $[\text{SiO}_2]$ concentration. Both models described the observed silica data equally well in the two streams (Figs. 5 and 6) when using the R^2 value as a measure of the goodness of fit. From a statistical point-of-view, however, the mixing model involving the logarithmic

Table 3. Variation in stream chemistry explained by discharge and two mixing models involving logarithmic (Hall 1970) and hyperbolic (Johnson et al. 1969) transformation of discharge (R^2 values in %). Results for normalized stream chemical data (see text) are shown below if improvement in R^2 was greater than 5%.

Site	Model ¹	Mg ²⁺ (n = 148) ²	SiO ₂	H ⁺ (n = 176) ³
<u>Harp 4</u>	C vs. q	45.1 58.2	52.7 61.5	66.9
	C vs. log (q) (Hall 1970)	59.6 73.7	81.4	54.6
	C vs. 1/(1+ β q) (Johnson et al. 1969)	59.0 73.7	81.7	67.8
<u>Plastic 1</u>	C vs. q	n.s.	38.5 51.3	24.2
	C vs. log (q)	n.s.	73.3	57.1
	C vs. 1/(1+ β q)	n.s.	72.0 81.0	59.0
<u>Paint 1</u>	C vs. q	n.s. 8.5	n.s.	30.4
	C vs. log(q)	n.s. 10.6	n.s.	28.8
	C vs. 1/(1+ β q)	n.s. 9.6	n.s.	33.6

¹ for estimates of β in Johnson model see Table 4

² n = 128 in Paint 1

³ n = 149 in Paint 1

transformation of discharge (Hall 1970) must be considered superior to the Johnson model, as it does not require an additional optimization parameter (β). Although β was an essential component in the derivation of the Johnson model, it is not well-determined, (i.e. the confidence intervals obtained for β are relatively wide compared to C_s and C_a (Table 4)), indicating that the Johnson model is not very sensitive with respect to β . The derivation of the mixing model after Hall (1970), on the other hand, is based on assumptions which are too specific to be tested and is therefore difficult to conceptualize.

Hooper (1986) argued that the physical interpretation of the Johnson model had to be modified since the factor β , which Johnson et al. defined as the ratio of residence time to field capacity of the watershed (i.e. a hydrologic constant), varied for several ions studied in the Hubbard Brook watershed, N.H. He pointed out that β may depend on the chemical properties of the solute (e.g. higher "effective" residence times (greater β) for ions which undergo ion exchange and are biologically active). Hooper concluded that the model should be viewed as an empirical model not one that describes physical or chemical mechanisms. Nevertheless, the Johnson model was thought to provide a good basis for comparison of hydrological and geochemical processes in the different watersheds when comparing its performance using solutes that behave similarly. Silica was chosen for comparison since it is believed to be relatively conservative in the sense that it quickly reaches solution equilibrium and thereafter does not interact greatly much with soil and biota

According to the derivation of the model after Johnson et al. (1969), the constant (C_a) in the regression model expresses the solute concentration level which pedologic processes are

able to sustain during periods of rapid replacement of soil water by rain water (non-equilibrium soil concentration). In the Harp 4 and Plastic 1 streams, this regression parameter was 2.1 and 2.2 mg/l respectively (Table 4; Figs 5 and 6) suggesting that the rates of silica release from the soils under non-equilibrium conditions should be very similar in both catchments. Johnson et al. (1969) found very similar C_a values for silica in small mountainous headwater streams at Hubbard Brook, N.H. (1.4-1.8 mg/l). The fact that such C_a values were still several magnitudes higher than the concentration found in the precipitation supports a compensating, fast chemical reaction within the soil. The phenomenon that silica can be rapidly picked up by infiltrating event water has been documented both in studies using stream response (Kennedy et al. 1986; Wels et al. 1988b) as well as soil leaching experiments (Bricker et al. 1968; Kennedy 1971).

The regression coefficient ($C_o - C_a$) expresses the difference between an equilibrium concentration in stored soil/groundwater C_o achieved during periods of baseflow when sufficient time is provided for geochemical processes to reach equilibrium and the above discussed non-equilibrium concentration C_a (Johnson et al. 1969). The larger regression coefficient obtained for Harp 4 (Table 4) suggests that the equilibrium $[SiO_2]$ in the soil provided by slow weathering processes is higher in this basin ($C_o = 5.7$ mg/l) than in Plastic 1 ($C_o = 4.7$ mg/l). This could result from the much deeper soils with well developed mineral horizons in Harp 4 where silicate weathering can occur.

Table 4. Optimized parameters and their 95% confidence intervals for Johnson mixing model applied to various stream solutes.

Site	Parameter ¹	Mg ²⁺ (n = 148) ²	SiO ₂	H ⁺ (n = 176) ³
<u>Harp 4</u>	C _δ	0.52±0.07	3.57±0.3	-9.77±8.9
	C _a	0.71±0.08	2.14±0.3	10.1±9.1
	β	0.54±0.40	0.62±0.3	0.2±0.02
<u>Plastic 1</u>	C _δ	n.s.	2.54±0.3	-29.7±3.7
	C _a	n.s.	2.20±0.2	47.2±1.5
	β	n.s.	2.12±1.1	2.66±1.3
<u>Paint 1</u>	C _δ	n.s.	n.s.	-7.2 ±6.0
	C _a	n.s.	n.s.	10.1 ±6.2
	β	n.s.	n.s.	0.06±0.1

¹ C_δ (= C_o-C_a) and C_a in mg/l for silica and magnesium and in μg/l for hydrogen - β in d/mm.

² n = 128 in Paint 1

³ n = 149 in Paint 1

Differences in the optimization parameter β for Plastic 1 and Harp 4 (Table 4), determined from the silica mixing models, followed an expected trend considering general differences in basin characteristics. Plastic 1 with its shallow overburden (< 1 m) was expected to have a much smaller capacity to store soil/groundwater than Harp 4 with its deep surficial deposits (Table 1). The hydrologic response of the Plastic 1 catchment to a melt event should, therefore, be much more rapid than Harp 4 due to the shorter residence times for water moving through the system.

Using the same mixing model for several steep mountainous headwater catchments in the Hubbard Brook Experimental Forest, N.H., Johnson et al. (1969) determined β values in the same range (1 d/mm) as optimized for Harp 4 and Plastic 1, although those catchments differ greatly from basins on the Canadian Shield in their relief. However, β was determined by trial and error and no confidence intervals for its estimates were given. A direct comparison may also be misleading since the solutes to which the model was applied may behave differently in each system studied.

Hydrogen

The observed pattern of increasing $[H^+]$ concentration with increasing discharge in all three watersheds (Fig. 1-3), has also been found for many other watersheds which receive acidic deposition (Johnson et al. 1969; Damsleth 1986; Sharpe et al. 1984; Lynch et al. 1986; Hooper 1986). Higher concentrations of hydrogen in stream water are to be expected during periods of high flow when a greater proportion of the flow is comprised of more acidic melt water. However, despite virtually identical average precipitation input values

at both sites, the concentration-discharge relationships in Harp 4 and Plastic 1 differed greatly in shape and intensity (Figs. 1 and 2).

The relatively poor performance of the hydrogen mixing models (Table 3) in describing this behaviour was not surprising considering the highly reactive nature of the hydrogen ion. The large scatter about the two mixing models suggests that processes other than physical mixing alone play an important role in the $[H^+]$ stream response. The much higher standard error of all regression parameters for hydrogen for the Johnson model when applied to Harp 4, and the orders of magnitude smaller β value compared to the silica model of the same catchment (Table 4) also indicates that the mixing model may be particularly inappropriate for predicting hydrogen behaviour in the Harp 4 stream. The soil and groundwater in Harp 4 itself might be providing enough alkalinity to buffer hydrogen ions resulting in a greater decrease in $[H^+]$ in the stream than predicted by the model even if only mixing of melt and soil/groundwater is taking place.

In Plastic 1, this may not have been the case since soil/groundwater provides very little alkalinity to neutralize the added hydrogen ions. Therefore, the $[H^+]$ -discharge relationship in this basin may have more closely followed that of a less reactive solute such as silica. The fact that β obtained for silica and hydrogen in Plastic 1 are very similar supports this hypothesis. If one visualizes stream water simply as a mixture of soil/groundwater and melt water then the stream $[H^+]$ concentration in Plastic 1 which was very close to melt water values would suggest that the soil/groundwater reservoir in this catchment was completely exhausted during periods of high flow. However, isotope studies within the same basin suggested that soil/groundwater remained an important flow component throughout spring

runoff (Wels 1989). The hydrogen ions must be provided from another source than melt water alone. A centrally located swamp in Plastic 1 was found to release addition $[H^+]$ during spring runoff maintaining typically high $[H^+]$ in the stream (Wels et al. 1988a; Wels 1989).

The behaviour of hydrogen may also be more difficult to explain by mixing of two sources alone, since the supply of hydrogen by melt/rain water varies over time. As reported by Johannessen and Henriksen (1978) in Sweden and by Semkin and Jeffries (1986) in Central Ontario, a large proportion of the hydrogen load in a snowpack is released very early (preferential thaw-out) leading to very acidic melt water early in the melt season and less acidic melt water later on. During rain-on-snow events the pH of the rain must also be considered. Depending on the conditions of the snowpack, rainwater can percolate directly through the snowpack and contribute to streamflow.

Whether the mixing models were applied to silica, magnesium or hydrogen, greater than 20% of the variation in stream solute concentration remained unexplained. This might indicate the inappropriateness of simple mixing concepts for explaining the hydrological and geochemical behaviour of these solutes. Mixing models perhaps over-simplify hydrological and biogeochemical processes considerably by assuming constant concentrations for ground/soil water and melt water and complete mixing of both components. These assumptions are questionable and depend on the solute basin characteristics. Complete mixing of melt water with soil/groundwater is only possible if all melt water infiltrates deeply enough to reach the water table, or the two components mix only and completely in the stream channel. This implies that saturated overland flow and shallow subsurface

flow of the input water (as rain or melt) is negligible. This is an unreasonable assumption in Shield catchments such as Plastic 1 where these flowpaths may be important particularly during periods of high flow.

Furthermore, the rate of dissolution from soil exchange and mineral weathering may differ depending on soil horizon and contact time with the meltwater. This has been suggested for Si and Mg in podzolic soils from the Plastic 1 basin (Wels 1989). The supply of these solutes to melt water is not constant in space and time which complicates the interpretation of mixing-models. Moreover, the flow paths of the infiltrating melt water are not considered.

Other factors may also be responsible for scatter in the mixing model:

- 1) hydrological and biogeochemical processes leading to a change in stream chemistry which are not directly related to discharge;
- 2) spatial heterogeneity even in small catchments, where different source areas are contributing at different times (Walling and Webb 1980);
- 3) hysteresis effects resulting in a lag in stream chemistry response to a storm event (O'Connor 1976; Walling and Webb 1980);
- 4) temporal trends in the source of the solute (e.g. a reduction in hydrogen from emissions);
- 5) data uncertainty caused by sampling errors, incompleteness and/or non-representativeness of sampling (Montgomery and Sanders 1986).

3.3 Summary

Paint 1 showed no clear concentration-discharge relationships, which may largely reflect the influence of a central pond on spring runoff and associated stream chemistry. In Harp 4, significant differences in Si, Mg and H^+ concentrations of the soil/groundwater and melt water resulted in decreasing Si and Mg concentrations, and increasing H^+ concentrations with increasing discharge. Plastic 1 showed a similar dilution pattern for silica, however, magnesium was not related to discharge probably due to an insufficient difference between baseflow and melt water Mg concentrations. Hydrogen concentrations in the Plastic 1 stream were affected little by discharge volume.

The mixing models (which assumed complete mixing of only two components) described the behaviour of Mg and Si better than a linear concentration-discharge relationship. The mixing models performed best for silica in Plastic 1 and Harp 4. Both mixing models explained equally well the variation of $[SiO_2]$ during spring runoff (72-80%). The mixing model given in Johnson et al. (1969) did not provide a better fit than the mixing model described in Hall (1970), despite the use of an additional optimization parameter. The similar dilution patterns for silica in Harp 4 and Plastic 1 suggested that the principal hydrological mechanisms may be similar in these catchments. A higher rate of silica dissolution in Harp 4 may have been a result of better developed mineral soil horizons and greater depth of the overburden.

4.0 PREDICTING STREAM SOLUTE BEHAVIOUR FROM FLOW PARAMETERS USING MULTIPLE REGRESSION ANALYSIS

When applying multiple regression analysis, several other flow variables were used to try and improve the concentration-discharge relationships. In addition to flow magnitude (q) already used in the mixing models, antecedent flow, absolute and relative change in flow and rise/fall of the hydrograph were also incorporated into the regression model.

4.1 Data Analysis

The flow variables used and their transformations are listed in Table 5. The wetness of the basin expressed through antecedent flow (X_2) is believed to influence the infiltration rates of precipitation and consequently the amount of surface runoff (Ledbetter and Gloyna 1964). A large increase in flow (X_3) may indicate a larger contribution of storm flow with a chemical composition closer to precipitation than to groundwater, analogous to the concept of quickflow and delayed flow (e.g. Pionke et al. 1972). The relative change in flow (X_4) may also indicate changes in flowpaths independent of the flow magnitude. Although the total volumes involved may be small, a change in stream chemical concentration can be expected. A dummy variable (X_5) was introduced to account for a possible hysteresis or lag effect (e.g. Walling 1974), resulting in differing concentrations on the rising and falling limb of the hydrograph.

Flow magnitude and antecedent flow were log transformed so that extreme values were not overemphasized. All independent variables were tested for collinearity (see Appendix).

Table 5. Independent flow variables used for multiple regression on stream solute concentration.

Variable	Unit	Transformation
X ₁ flow magnitude ¹	mm/d	log
X ₂ antecedent flow ²	mm/7d	log
X ₃ absolute change in flow ³	mm/d	none
M ₄ relative change in flow ⁴	unitless	none
H ₅ rise/fall of hydrograph ⁵	unitless	none

¹ mean daily specific discharge at day of sampling (q)

² cumulative q of seven days prior to sampling

³ absolute difference between q at day of sampling and q at day prior to sampling

⁴ ratio of q at day of sampling to q at day prior to sampling; inverse ratio on descending limb of hydrograph

⁵ dummy variable dividing the population into observations on ascending and descending limb of hydrograph

Flow magnitude (X_1) and antecedent flow (X_2) were found to be highly correlated ($R^2 \approx 0.8$). Antecedent flow (X_2) was therefore excluded from the analysis. All remaining flow variables were used in a multiple regression on the stream solute concentrations. The partial regression coefficient of each independent variable, was tested for its significance ($p < 0.001$) using Student's t-test (Sokal and Rohlf 1981; p. 637). Only those significant independent variables were used in the final regression model.

Multiple regression analysis was applied to Harp 4 and Plastic 1 only. Paint 1 was not considered because of the poor solute vs. discharge relationships suggesting little influence of hydrology on its stream solutes. Although it was recognized that stream solute concentrations normalized to yearly means may yield better relationships than original values, they were not used in this analysis simply because original values were thought to be more relevant for predictive purposes. A normalization procedure may camouflage changes in solute concentrations which might be attributed to processes reflected by one of the independent variables.

Two separate regression analyses were performed. The first, included all observations regardless of the discharge ('all flow'). The second used only observations made during 'high flow' ($q > 2.5 \text{ mm/d}$). Periods of high flow are of particular interest since the 'system' catchment is in a non-equilibrium state and often produces extreme stream solute concentration which might be of environmental concern (e.g. spring acid pulse).

Table 6. Summary of multiple regression analysis of selected flow variables on stream concentration of magnesium, silica and hydrogen ion considering all observations ('all flow analysis').

Site	Solute ¹	Selected Independent Variables ²	R ² (in %)
<u>Harp 4</u>	Mg ²⁺ (145)	X ₁	59.6
	SiO ₂ (144)	X ₁	81.4
	H ⁺ (178)	X ₁ , X ₃ , X ₅	60.3
<u>Plastic 1</u>	Mg ²⁺ (150)	n.s.	n.s.
	SiO ₂ (147)	X ₁	83.3
	H ⁺ (178)	X ₁ , X ₃ , X ₅	66.9

¹ degrees of freedom in brackets

² in order of significance

4.2 Results

The regression analysis on the entire flow range ('all flow analysis') revealed some similar results for Si and H^+ in the two watersheds studied. The independent variables selected for the silica and hydrogen models and their goodness of fit (expressed as R^2) were very similar in Harp 4 and Plastic 1 (Table 6). In the case of silica in both catchments and magnesium in Harp 4, only flow magnitude was identified as an important flow variable. No other introduced flow variable could improve the regression model significantly.

For hydrogen, flow magnitude (X_1) was the dominant independent variable. However, absolute change in flow (X_3) and rise/fall of hydrograph (X_5) could explain some of the variation not accounted for by X_1 (Table 6). The hysteresis variable showed a similar negative relationship in Harp 4 and Plastic 1, indicating that $[H^+]$ was generally lower on the rising limb than on the falling limb of the hydrograph. Absolute change in flow (X_3) was positively related to $[H^+]$ in Harp 4, but negatively correlated to $[H^+]$ in Plastic 1. The independent variables used described hydrogen behaviour in the streams less successfully than the silica.

In order to demonstrate the strengths and weaknesses of these simple regression models, silica and hydrogen (expressed as pH) were simulated for the 1984 spring runoff in Harp 4 (Fig. 7) and Plastic 1 (Fig. 8). In both watersheds the regression models portrayed the dominant changes in silica and pH, usually observed during periods of high changes in flow. The silica response to changes in flow was drastic in both catchments (Figs. 7 and 8). Yet, particularly in Harp 4, the silica model failed to simulate those considerable changes in

[SiO₂] which were not associated with large changes in flow, e.g. early during the melt season (e.g. day 58-75; Fig. 7). The stream pH in Plastic 1 was not only much lower than in Harp 4 but also showed much less variation during periods of high flow (Fig. 8). The hydrogen model overestimated the recovery from pH depressions at peak flows in both streams (e.g. day 58-75; Figs. 7 and 8) despite the incorporation of a hysteresis dummy variable.

The regression models developed for high flow periods alone differed greatly between the two catchments with respect to the variables selected as well as variation explained by the model (Table 7). In Harp 4, flow magnitude remained the dominant flow variable for all stream solutes (Table 7). Changes in [SiO₂] and [Mg²⁺] could not be explained by the other variables even when considering only high flow observations. However, the coefficients of determination (R²) for the high flow models of silica and magnesium were significantly lower (30-35% less explained variance) than in the all flow analysis. In contrast, the inclusion of antecedent flow (X₂) and relative change in flow (X₄) into the hydrogen models in addition to flow magnitude (X₁) yielded R² values in Harp 4 similar to those of the respective all flow models (Tables 6 and 7).

In Plastic 1, flow magnitude (X₁) was not included in the high flow model. For silica, the only high flow model with an R² close to 50%, antecedent flow (X₂) replaced flow magnitude as the dominant flow variable. In general, stream solute response during periods of high flow appeared to be much more difficult to predict. Although a greater number of independent variables were important less variation was actually explained.

Table 7. Summary of multiple regression analysis of selected flow variables on stream concentration of magnesium, silica and hydrogen ion considering high flow observation ('high flow analysis').

Site	Solute ¹	Selected Independent Variables ²	R ² (in %)
<u>Harp 4</u>	Mg ²⁺ (65)	X ₁	29.0
	SiO ₂ (65)	X ₁	44.5
	H ⁺ (82)	X ₁ , X ₂ , X ₄	64.4
<u>Plastic 1</u>	Mg ²⁺ (76)	n.s.	n.s.
	SiO ₂ (73)	X ₂ , X ₄ , X ₅	48.4
	H ⁺ (76)	X ₅	17.1

¹ degrees of freedom in brackets

² in order of significance

4.3 Discussion

'All Flow' Case

In general, flow magnitude was the most important flow variable for explaining solute behaviour studied in Plastic 1 and Harp 4. Silica and possibly magnesium which are mainly supplied by rock weathering and are therefore found in much higher concentrations in soil/groundwater than in the melt water show this best. For these solutes, none of the other flow variables could significantly explain the remaining variation indicating that the volume of runoff was the dominant factor in the dilution process.

Comparing these results to those from other studies proved difficult. Different flow variables were often used and [TDS] as measured by electric conductivity was often used instead of specific solutes (O'Connor 1976; for review). Total dissolved solids and its response to changes in flow, however, might be more difficult to interpret, although the dilution pattern generally observed for TDS suggests that it behaves similarly to silica and magnesium. Nevertheless, its dependence on other flow characteristics may differ. In general, the introduction of flow variables other than discharge to explain variation in TDS (e.g. antecedent discharge (Ledbetter and Gloyna 1964), absolute change in flow (Pionke et al. 1972) or flow components (Walling 1974)) did not improve the predictive power of the regression models greatly. In the case of solutes such as TDS or silica, for which the relationship with discharge alone is already very significant, it may be difficult to improve the predictive power of the model by further consideration of flow variables which are somewhat related to discharge.

The importance of discharge in the all flow model for hydrogen may reflect the influence of flow rates on neutralization processes occurring within the soils of the two basins. In contrast to the silica models, absolute change in flow (X_3) and rise/fall of hydrograph (X_5) could further explain some of the remaining variation and may be attributed to the non-conservative nature of hydrogen. For example, the selection of the hysteresis variable for the hydrogen model (X_5), agrees well with the observation that hydrogen (pH) values return low baseflow levels more slowly than discharge itself (e.g. Bottomley et al. 1984; Lynch et al. 1986). The consistent selection of X_3 and X_5 in the hydrogen models at both sites lends some confidence to their importance, however, their use for prediction is rather limited since these variables did not explain more than 10% of the variation in $[H^+]$. A variable which better reflects chemical interactions is needed to substantially improve the hydrogen models. A more flexible 'hysteresis variable' which considers volume of the previous storm or the time elapsed since peak flow may be more useful.

'High Flow' Case

In Harp 4, flow magnitude (X_1) remained the dominant flow parameter for all solutes studied, when baseflow samples were removed from the analysis. The dominance of this variable is also expressed in the stability of its regression coefficient which changed very little from all to high flow models. In contrast, flow magnitude did not remain dominant in Plastic 1, once baseflow samples were excluded from the analysis. The limitations of extrapolating from the general 'all flow' model which describes changes from base to high flow, to specific processes during high flow can clearly be seen in the case of hydrogen in

Plastic 1. Scatterplots of hydrogen already indicated that the decrease in $[H^+]$ with increasing discharge is restricted to a small range of flow. During high flows no relationship of hydrogen with discharge was apparent (Fig. 2 and 3). As a result no flow variable could explain much of the variation in hydrogen when high flow conditions only were examined. The silica 'high flow' model in Plastic 1 differed from the 'all flow' model with respect to the variables selected, although the actual silica simulations using either model were similar (Fig. 9). The selection of antecedent flow (X_2) and relative change in flow (X_4) for the silica model during high flow periods confirm the results of a detailed previous investigation of silica in the same catchment (Wels 1989). Once high baseflow concentrations have been diluted to a relatively low level by water passing through the soil, further dilution is accomplished by water that has had no contact with the mineral horizons of the soil. High antecedent discharge and rapid change in flow may promote shallow subsurface flow and saturated overland flow and thus lead to a further decrease in $[SiO_2]$ in the stream during periods of high flow.

A visual comparison of 'all flow' and 'high flow' simulations for silica in Plastic 1 which differed greatly in their composition of X as well as their coefficient of determination (R^2) showed that for various high flow periods, the models simulated the $[SiO_2]$ behaviour very similarly (Fig. 9). The slight improvement in the description of $[SiO_2]$ by the 'high flow' model (in terms of R^2) did not seem to justify its use over the 'all flow' model for predictive purposes, considering the general applicability of the 'all flow' model to the entire flow range (i.e. to continuously simulate/predict $[SiO_2]$ for an entire spring runoff).

4.4 Summary

Results of the all flow analysis demonstrated the dominant influence of flow magnitude on changes in stream solute concentration from base to high flow in Plastic 1 and Harp 4. For silica and magnesium, only flow magnitude could explain the stream solute behaviour. For hydrogen, absolute change in flow and fall/rise of hydrograph were suggested as also important, however, they did not contribute much to the overall performance. The 'all flow' models described changes from baseflow to high flow well and offer a simple means for the simulation of the general behaviour of these stream solutes during spring runoff.

The 'high flow' analysis served to test the use of 'all flow' models with respect to periods of high flow. In Harp 4, the 'all flow' and 'high flow' models did not differ significantly. Flow magnitude remained the dominant flow variable, suggesting that dilution is also the main process pertaining to a change in stream solute concentration during periods of high flow in this catchment. In Plastic 1, 'high flow' models differed greatly from the 'all flow' models. For silica, antecedent flow (X_2) and relative change in flow (X_4) replaced flow magnitude, although the simulation of $[\text{SiO}_2]$ using 'high flow' and 'all flow' models were similar during high flow periods. The scatter of hydrogen at elevated discharge could not be explained significantly by any flow variable except rise/fall of hydrograph. It can be concluded that, although both catchments exhibit similar overall changes in stream chemistry from baseflow to high flow, detailed responses during high flow events differed considerably.

5.0 STREAM SOLUTE BEHAVIOUR DURING SELECTED STORM EVENTS

Several authors have pointed out the complexity of stream solute response during an individual storm event (Walling 1974; O'Connor 1976; Foster 1978). Storm characteristics which affect stream chemistry may not have been adequately addressed through the flow variables previously used, as they did not consider the 'hydrological context' of a storm event. In this chapter, the importance of storm characteristics will be tested by relating changes in stream solute concentration observed during the course of selected storm events, to some of the hydrological and meteorological storm conditions.

5.1 Storm Analysis

The identification of individual storm events from the hydrograph was difficult due to the special conditions during snowmelt runoff in this area. Frequent freeze-thaw cycles combined with large rainstorms resulted in a very complex hydrograph for the spring runoff period. Several individual storms were commonly overlapping. The need for clearly defined storms in order to determine storm characteristics without ambiguity greatly reduced the number of storm events finally selected.

Runoff and stream chemical data were scrutinized in order to select all clearly defined single-peaked hydrographs for which detailed records of stream solute concentrations were available. A period of 'high flow' was considered a 'storm event' if maximum flow exceeded two times the pre-storm level (before rise of hydrograph). A minimum of 3.7 mm/d (10 l/s) at peak flow had to be exceeded. A total of 14 storms were found suitable for multiple

regression analysis. For 11 storms, pre-storm discharge could be considered base flow ($< 1.85 \text{ mm/d}$ or 5 l/s). The onset of storm was defined as the first day when Q surpassed baseflow level. In 3 storms, when pre-storm discharge had not recovered to baseflow values before rise of hydrograph, the onset of storm was defined as the first day of a rising hydrograph. The set of storm events covered a wide range of Q_{\max} ($4.77 - 29.23 \text{ mm/d}$). The number of days to reach peak flow ranged from three to eight which shows the relatively slow runoff response to rainstorm events during the melt period (see Appendix).

A consideration of the entire storm hydrograph was abandoned when problems were encountered in identifying the end of a storm in the complex pattern of spring runoff. Instead, only the rising part of the storm hydrograph was considered for the identification of storm characteristics. Although this restricts the identification of storm parameters, it is not an uncommon practice (Foster 1978). Preliminary investigations of our data set showed that the dominant changes in stream solute concentrations usually occurred at peak flow, and therefore are caused mainly by storm characteristics prior to and during peak flow. Seven independent variables were chosen encompassing hydrological and meteorological conditions at or previous to the storm event (Table 8).

The hydrological storm variables (X_1 - X_3) were obtained directly from the hydrograph. For the meteorological storm variables X_4 , X_5 , and X_6 monthly weather reports for Dorset/Ontario (Environment Canada 1980-1984) were used. Storm magnitude (X_1) was considered a summary measure indicating the amount of melt and rain that actually contributed to stream runoff. It was believed that with an increasing amount of water being flushed through the system the stream solute concentrations would approach their respective

Table 8. Independent storm variables considered for multiple regression analysis.

Variable	Unit	Transformation
X ₁ storm magnitude ¹	mm	log
X ₂ antecedent flow ²	mm	log
X ₃ storm intensity	mm/d	non
X ₄ storm precipitation ⁴	mm	non
X ₅ air temperature ⁵	°C	non
X ₆ season effect ⁶	days	non

¹ storm volume from rise of hydrograph to peakflow

² cumulative discharge of 10 days prior to rise of hydrograph

³ storm magnitude divided by # of days from rise of peak of flow

⁴ total amount of precipitation (rain only) fallen during storm event, i.e. from one day prior to rise of hydrograph until day of peak flow

⁵ average mean daily air temperature during storm event

⁶ days elapsed since onset of first melt in season

precipitation values. The wetness conditions in the basin prior to the onset of the event, expressed as antecedent flow (X_2), may influence the storm solute behaviour by altering the flowpaths of melt and rain water (see 4.1). The time frame in which the melt/rain water is delivered to the stream, (i.e. storm intensity (X_3)), may also be an important storm characteristic. A high intensity storm may produce more rapid surface flow than subsurface flow. Storm precipitation (X_4) was considered for analysis in order to specifically examine the influence of rain on solute concentrations during melt events. Rain-on-snow events can be expected to differ from melt events in that flow rates may be typically higher and more rain (water with a chemical composition often quite different from melt water) may contribute to storm flow. The mean daily air temperature for a storm event may to some extent reflect the amount of melt (all storms had an initial snowcover) and its influence on the storm solute behaviour. The season effect (S_6) may account for differences in storm solute behaviour which are not a result of the storm itself but the time of its occurrence in the context of the entire spring melt. Such differences in the chemical composition of the stream water may be a result of an inconsistent supply (e.g. hydrogen ions in snowpack, silica release from weathering) or uptake (e.g. biological uptake of silica) over the course of spring runoff.

Multiple regression analysis was applied to the stream solutes silica and hydrogen which have previously been shown to be subject to considerable dilution decreases and concentration increases respectively during periods of high flow. Only the Plastic 1 catchment was considered for this analysis since (1) the melt hydrographs were relatively easy to define, and (2) the sampling frequency had been the highest which facilitated the interpretation of the stream solute behaviour during storm events.

The stream solute response of a storm event can be expressed either as an absolute change or a relative change. In the former case the highest/lowest concentration for each storm event is considered without reference to pre-storm concentration levels (GROUP A = extreme value). Values for GROUP A were obtained by selecting the lowest $[\text{SiO}_2]$ and the highest $[\text{H}^+]$ at or closest to peak runoff. A 'relative change' describes the deviation of this minimum/maximum concentration from the pre-storm concentration. (GROUP B = range value). The concentration of the sample closest to the onset of the storm was chosen as the reference (pre-storm concentration). Since samples had not been taken every day throughout the runoff season some pre-storm concentration values were from samples dating back more than one day, but not more than three days.

Stepwise multiple regression was employed to achieve a relatively high predictive power of the model while maintaining a reasonable level of significance. A STEPWISE FORWARD procedure was used (SAS 1985; p. 764). Before entering a new independent variable into the model, its F-statistic was calculated reflecting the contribution of the variable to the model. The model stopped entering new variables if the computed F-statistic did not have a significance level of greater than 0.05.

The independent storm variables X_1 and X_2 were log transformed for similar reasons as described in section 4.1.

5.2 Results

The independent storm variables were first tested for collinearity (see Appendix). Storm intensity was positively correlated with storm magnitude indicating that larger storms are generally also more intense. Storm air temperature (X_5) was also positively correlated with storm magnitude (X_1) whereas storm precipitation (X_5) was not. This agreed with thermodynamical considerations of snowmelt. The energy, supplied by precipitation to melt snow is much smaller than the energy supplied by heat; hence snowmelt events associated with high air temperature can be expected to produce highest runoffs during snowmelt. However, none of the above mentioned correlations were high enough ($R^2 > 0.8$) to justify the exclusion of a storm variable from the analysis.

For neither $[\text{SiO}_2]$ nor $[\text{H}^+]$, (whether expressed as an extreme or a range value), were more than two storm variables significant at $p < 0.05$ (Table 9). The predictive power of all the step-wise regressions was relatively low. Only one regression (absolute change in silica) could explain more than 60% of the variation of stream Si and H behaviour in 14 storms. The analysis further indicated that for both solutes the range value and the extreme value made a difference to the storm parameters chosen as important regressions using the extreme values explained more of the variation (50-80%) than the range values. Regression models of range values explained very little of the observed silica variation or were not at all significant for hydrogen.

Only air temperature (X_5) could explain some of the variation in maximum $[\text{H}^+]$ observed during the 14 storms (Table 9) but the relationship was inverse, (low $[\text{H}^+]$ at higher air

Table 9. Summary of stepwise multiple regression analysis of selected storm variables on stream concentration of silica and hydrogen ion in Plastic 1. Group A indicates an absolute change in stream solute concentration during a storm event, Group B a change relative to pre-storm levels (see text).

Group	Solute ¹	Selected Storm Variables ²	R ² (in %)	F-value
GROUP A	SiO ₂ (11)	X ₁ , X ₆	76.1	18.9/6.8
	H ⁺ (12)	X ₅	52.8	13.4
GROUP B	SiO ₂ (12)	X ₄	37.5	7.19
	H ⁺ (14)	n.s.	n.s.	n.s.

¹ degrees of freedom in brackets

² in order of significance

temperatures at peak flow). The minimum $[\text{SiO}_2]$ during storm events could be explained fairly well by storm magnitude (X_1) and season effect (X_6) (Table 9). The regression model suggested that the lowest concentrations in stream silica could be expected during larger storms later in the season. Storm magnitude, however, was not an important flow variable in explaining deviations of the extreme value from pre-storm concentrations (group B). Only precipitation was found to be statistically significant ($p < 0.05$) for silica in this group, suggesting that high rainfall during a melt storm event leads to higher decreases in silica from pre-storm concentrations (Table 9).

Extreme silica values observed at peak flow were not related to their pre-storm concentrations. The change in $[\text{SiO}_2]$ from pre-storm to peak flow level was rather dominated by the pre-storm value ($R^2 = 0.78$) than by the storm conditions. High pre-storm values which are more likely to produce a greater change during the storm event, were mainly found in the early melt events when pre-storm flow is very low (baseflow). Those early events are less likely to produce high runoffs since storage demands have to be met first. Storms with high storm magnitude and antecedent flow, although yielding very low extreme values may not produce the highest deviations from pre-storm concentrations.

5.3 Discussion

Lynch et al. (1986) provided regression models for extreme values of pH, alkalinity, and total acidity observed during 18 summer rain storms. These models explained between 80% and 94% of the variation. However, by themselves, none of the individual storm variables used showed a strong relationship with the respective solute concentration. This made

interpretation of the models difficult. To avoid these problems, the addition of a storm variable into our model was dependent on improvement to the model as determined by the F-statistic. Although the significance level chosen ($p < 0.05$) was very moderate, not more than two independent flow variables were accepted into any model. This may indicate that storm characteristics have only a limited influence on the storm solute behaviour in Plastic 1. However, it may also be an indication that the storm characteristics had not been defined appropriately or that the number of observations were not sufficient to show the overall trends. Multiple regression analysis of such a small set of storm events can hardly be used for rigid hypothesis testing and/or a desired in-depth interpretation of the physical processes involved during melt storms. With respect to the selection of the storm variables it has to be considered that they were solely derived from mean daily hydrographs and daily meteorological data which were not collected at the site and/or specifically for this study. These variables have the advantage that they are readily available, however, they may not be sensitive enough to adequately describe storm characteristics. Moreover, a better knowledge concerning the snowpack conditions and the contribution of snow in a given precipitation event would be very useful in the context of snowmelt runoff.

A comparison of regression models for the hydrogen and silica in groups A and B suggested that during snowmelt runoff in Plastic 1, storm characteristics are more likely to predict extreme values than changes from concentration values preceding the storm. Foster (1978) compared regression models of extreme and range of storm concentrations for various solutes (Ca^{2+} , Na^+ , Mg^{2+} and Cl^-) during 33 rain storms. He found that 'range of discharge' replaced 'total discharge' as the single dominant storm variable for the model of range values. In all cases, levels of explained variance were at least 10% lower than models

applied to the extreme solute concentration. This supports the hypothesis that extreme values are more dependent on storm characteristics than the range values, implying a certain independence of an extreme concentration obtained during a storm event from its pre-storm value.

Storm magnitude was found to be the dominant independent flow variable for minimum silica (see F value in Table 9). This is consistent with previous results (Sections 3.0 and 4.0) which have shown that dilution was the key process determining silica concentrations in the stream. The dominance of storm magnitude for Si_{min} is also consistent with results obtained by Foster (1978) for other weathering products. By applying the same analysis to 33 rain storms, he found maximum storm discharge to be the only significant storm variable to explain variation of minimum electric conductivity values and the dominant variable to explain variation of minimum values of Mg^{2+} , Na^+ and Ca^{2+} . The consistency of the results suggests that processes leading to the dilution of such solutes are similar during spring melt events and summer rain storms. However, antecedent flow was not selected in the storm models, although it was a dominant flow variable in the silica model for high flow periods in Plastic 1 (Tables 7 and 9).

Air temperature was identified as the dominant storm variable for explaining the extreme storm $[H^+]$. The negative relationship indicated that high increases in $[H^+]$ were associated with low air temperatures. Storms with low air temperatures usually occurred early in the spring and were smaller in magnitude. These storms might be more susceptible to elevated hydrogen levels because hydrogen is preferentially transported during this early period of melt (see section 3.3). By the time the major runoff occurs, the snowpack might be so

depleted in hydrogen that melt water effectively acts as a diluent. High air temperatures may further increase the chance of removal of hydrogen through biogeochemical processes such as cation exchange and weathering in the soil or uptake by organisms. As a result the hydrogen response to a melt event may well differ from its behaviour during summer rain storms since the source of hydrogen differs in the two cases. Lynch et al. (1986), found that storm size was the most highly correlated storm variable to changes in $[H^+]$. Quickflow ranked second. Both were positive correlations. Our results, however, suggest that during storm events dominated by melt water this relationship may be reversed since maximum $[H^+]$ concentrations are more dependent on its presence in the melt water than on the storm magnitude.

5.4 Summary

The analysis of selected storm events in Plastic 1 has shown that extreme values observed at or close to peak flow were more closely related to storm characteristics than the deviation from pre-storm concentration. Storm silica concentrations were negatively correlated with storm magnitude and time since the onset of melt, whereas hydrogen concentrations were highest during storm events associated with colder air temperatures. Since it can not be safely concluded how representative those results are, a more detailed sampling of storm events would be desirable which would allow the identification of more appropriate storm characteristics.

6.0 CONCLUSIONS

The relationships of dissolved silica, magnesium and hydrogen with hydrology during spring runoff were investigated in three small Shield headwater streams. Concentration-discharge relationships were first examined. In Paint 1, none of the three studied stream solutes showed a good relationship with discharge. A centrally located beaver pond, covering 10% of the drainage area, was believed to significantly influence stream flow and chemistry.

Very similar silica-discharge relationships were observed in Harp 4 and Plastic 1 which agreed well with mixing models conceptualizing the stream water as a mixture of soil/groundwater and melt water. A selection of a 'best' model was not possible as the two mixing models tested explained the variation in $[\text{SiO}_2]$ equally well (80-90%). Results suggested that the principal hydrological mechanisms may be very similar in those two catchments.

In Harp 4, Mg^{2+} was closely correlated with SiO_2 exhibiting a similar dilution pattern. In Plastic 1, Mg^{2+} was not related to discharge since the $[\text{Mg}^{2+}]$ levels observed in the soil/groundwater were not much higher than those in the melt water.

The mixing models did not describe the hydrogen behaviour as well as the behaviour of the weathering products SiO_2 and Mg^{2+} , particularly in Harp 4. This suggests that biogeochemical processes complicated the simple concept of the physical mixing of two components with constant $[\text{H}^+]$. Observed ranges in hydrogen were much smaller in Harp

4 than in Plastic 1 indicating that neutralization of hydrogen occurred at a much faster rate in Harp 4 or was based on different mechanisms/processes.

The influence of flow variables other than discharge on stream solute behaviour was then tested applying multiple regression analysis. The all flow analysis yielded very similar results in both Harp 4 and Plastic 1 again emphasizing that hydrogen behaves differently than the silica and magnesium as already suggested by the analysis of the concentration-discharge relationships.

Discharge (flow magnitude) was the only flow variable influencing the stream concentration of silica and magnesium whereas for hydrogen some of the residual variation could be explained by including the change in discharge and a hysteresis effect.

The behaviour of $[\text{SiO}_2]$ and particularly $[\text{H}^+]$ during periods of high flow were not consistent in the two catchments. Only in Harp 4, did discharge remain the dominant flow variable determining $[\text{SiO}_2]$ and $[\text{H}^+]$ concentrations. In Plastic 1, antecedent flow and relative change in flow better explained the silica variation at high flow. Hydrogen was poorly correlated with all hydrologic variables approaching melt water levels.

A study of individual storm events for Plastic 1 further suggested that early melt events had the greatest potential to produce extremely low pH values in the stream and that the lowest $[\text{SiO}_2]$ levels were observed later in the melt season and were associated with the highest flows.

We conclude from the study that hydrology plays a dominant role in influencing the stream chemistry in these small Shield headwater catchments during spring runoff. Differences in the buffering capacity of these systems can not be accounted for only by hydrologic differences.

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FIGURES

- Fig. 1** Concentration-discharge relationships for magnesium, silica, and hydrogen (pH) during spring runoff in Harp 4 (1977-1984).
- Fig. 2** Concentration-discharge relationships for magnesium, silica, and hydrogen (pH) during spring runoff in Plastic 1 (1980-1984).
- Fig. 3** Concentration-discharge relationships for magnesium, silica, and hydrogen (pH) during spring runoff in Paint 1 (1977-1984).
- Fig. 4** Silica versus magnesium during spring runoff in Harp 4.
- Fig. 5** Mixing models after Johnson et al. (1969) and Hall (1970) applied to silica during spring runoff in Harp 4.
- Fig. 6** Mixing models after Johnson et al. (1969) and Hall (1970) applied to silica during spring runoff in Plastic 1.
- Fig. 7** Silica and pH simulation during spring runoff 1984 in Harp 4 based on the multiple regression model.
- Fig. 8** Silica and pH simulation during spring runoff 1984 in Plastic 1 based on the multiple regression model.
- Fig. 9** Silica and pH simulation in Plastic 1 (1982 and 1984) based on the 'all flow' and 'high flow' model.

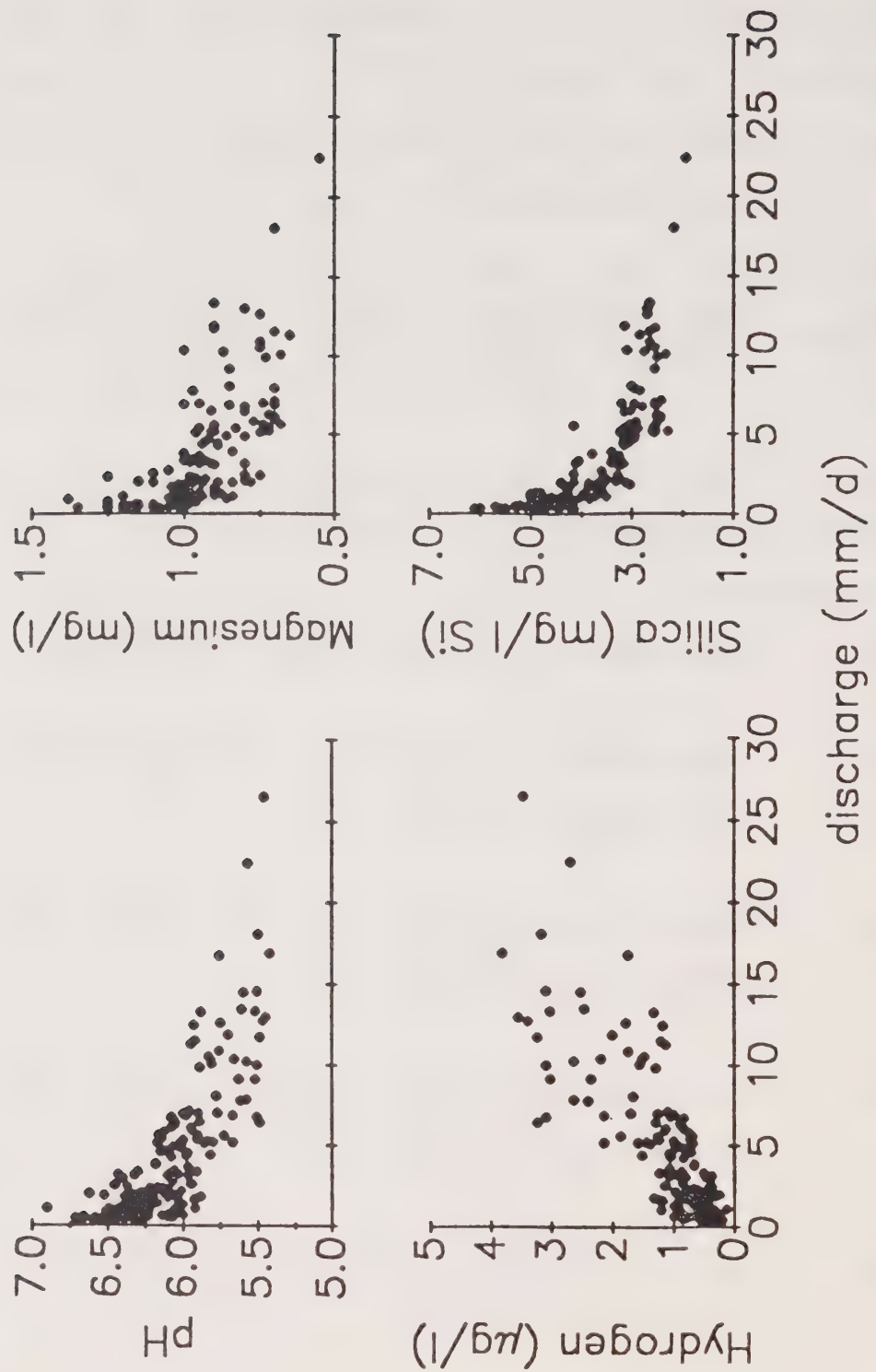


Fig. 1

Concentration-discharge relationships for magnesium, silica, and hydrogen (pH) during spring runoff in Harp 4 (1977-1984).

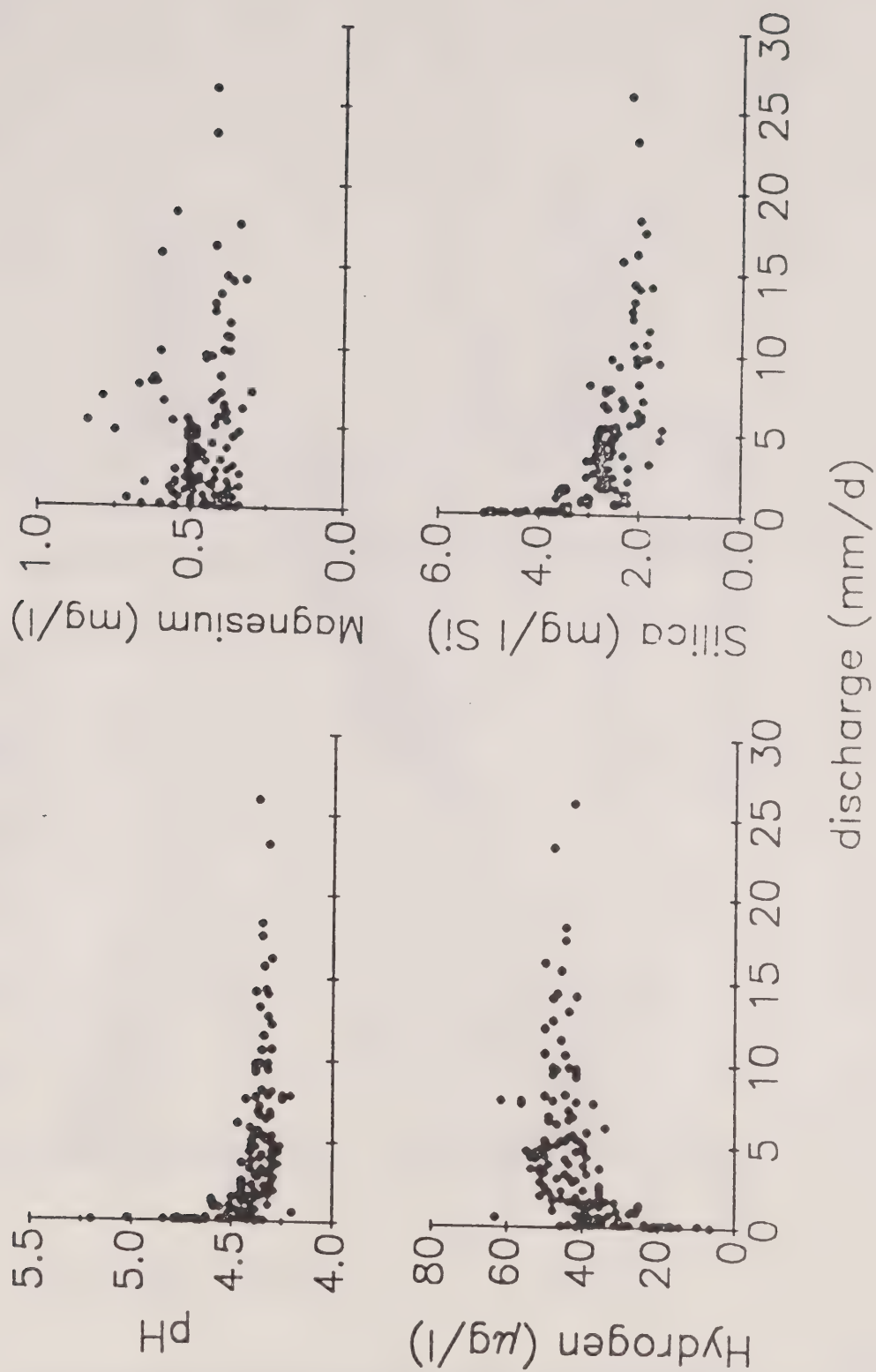


Fig. 2

Concentration-discharge relationships for magnesium, silica, and hydrogen (pH) during spring runoff in Plastic 1 (1980-1984).

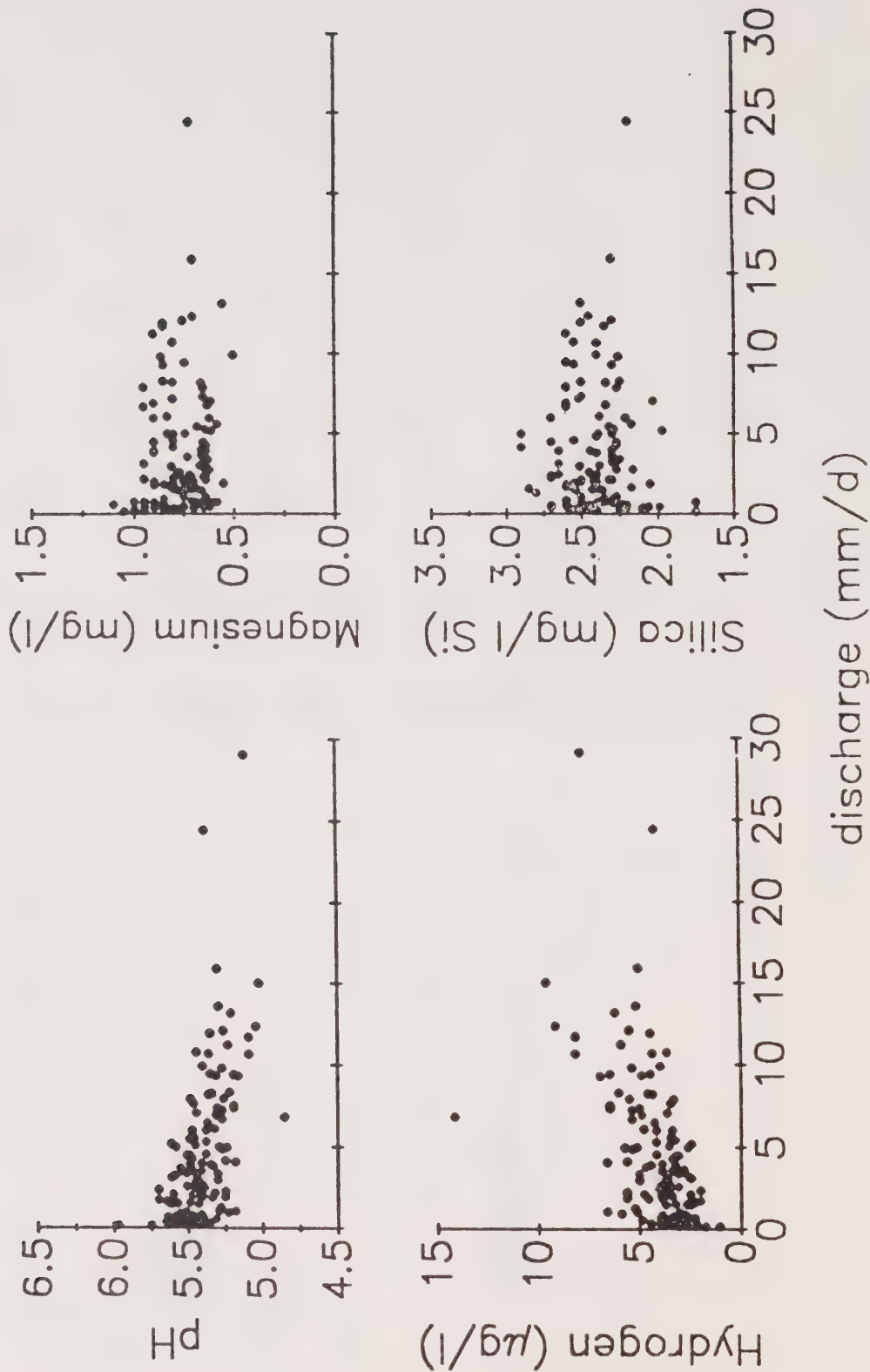


Fig. 3

Concentration-discharge relationships for magnesium, silica, and hydrogen (pH) during spring runoff in Paint 1 (1977-1984).

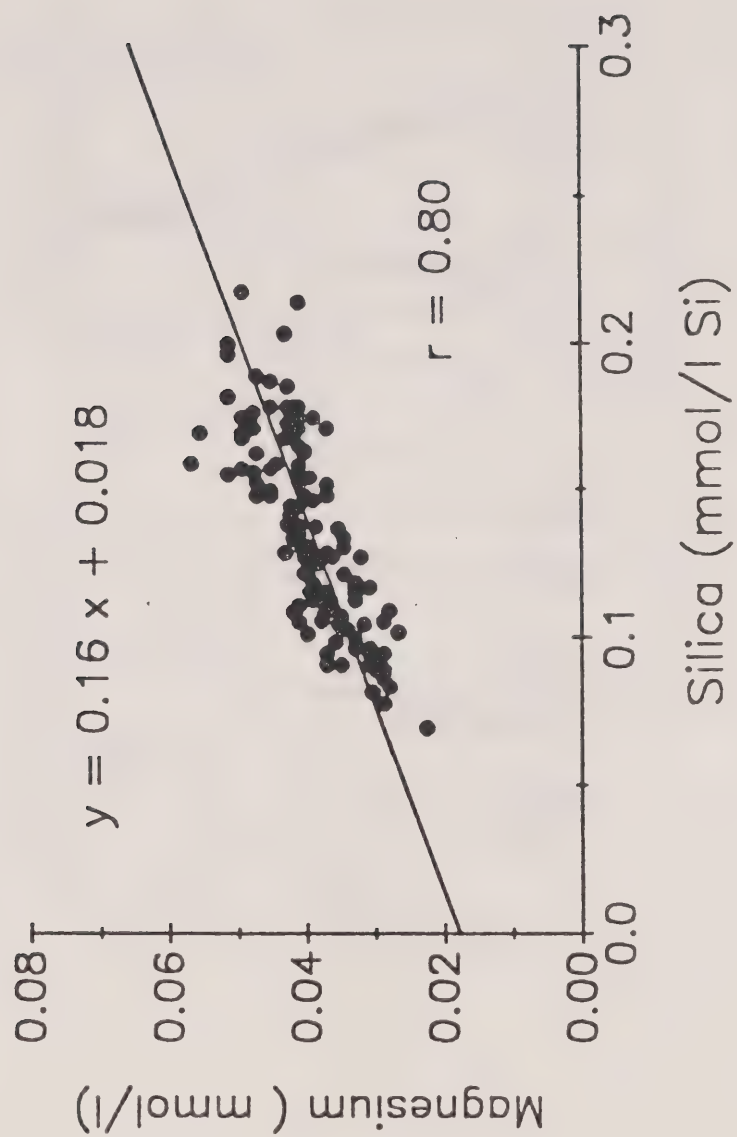


Fig. 4 Silica versus magnesium during spring runoff in Harp 4.

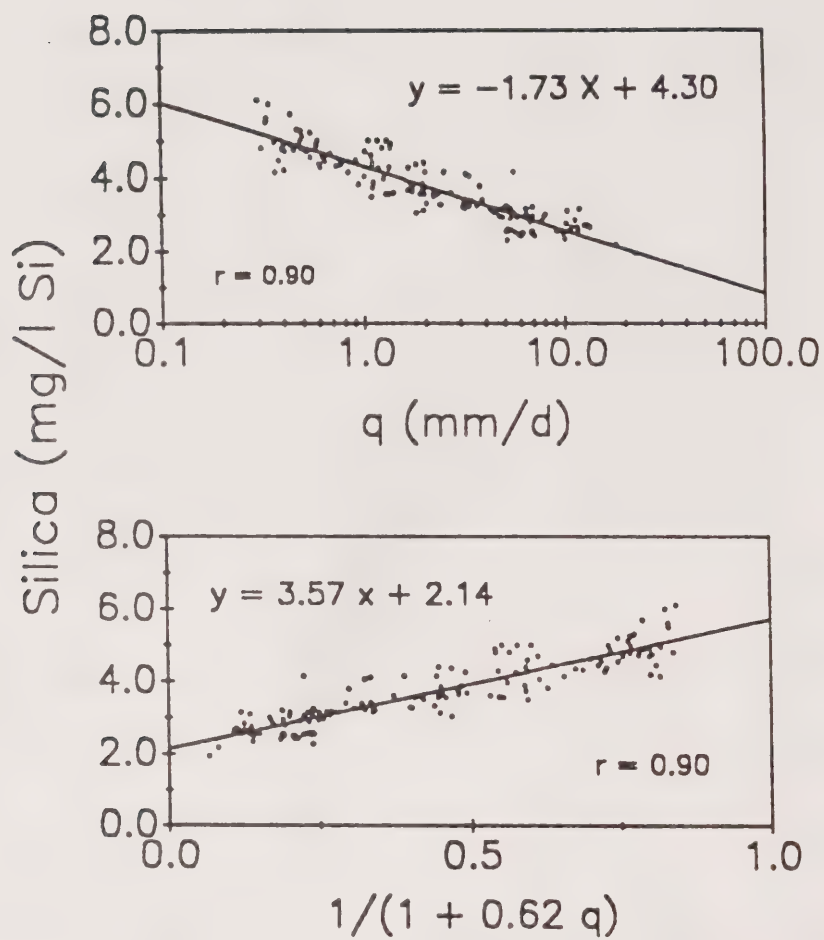


Fig. 5

Mixing models after Johnson et al. (1969) and Hall (1970) applied to silica during spring runoff in Harp 4.

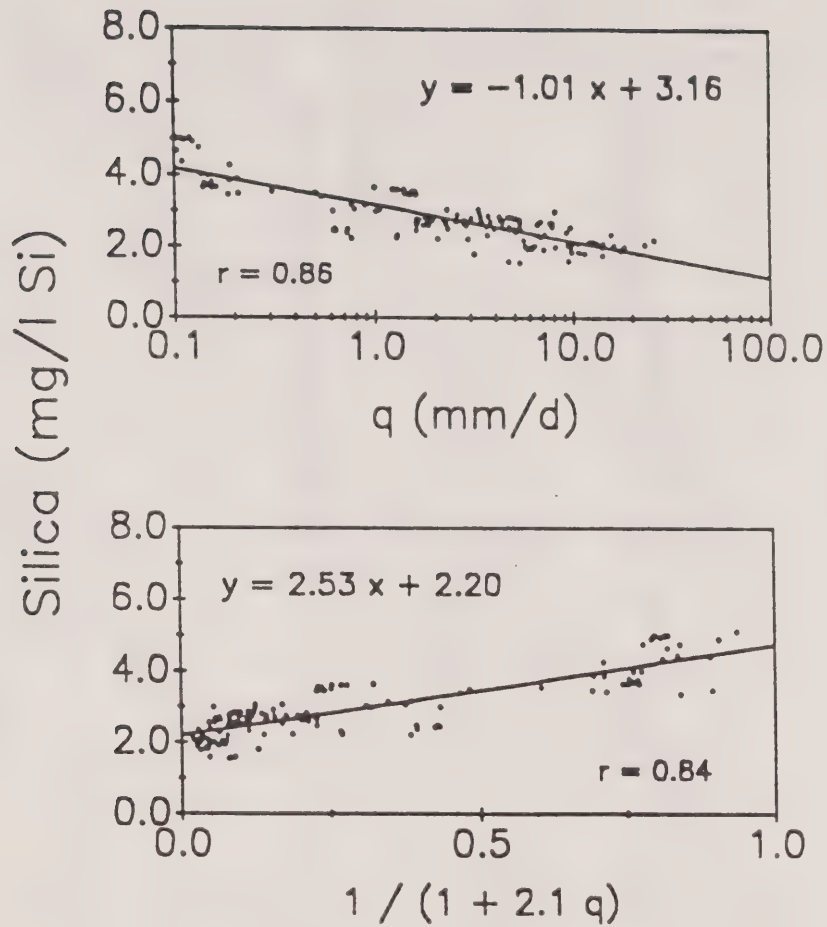


Fig. 6 Mixing models after Johnson et al. (1969) and Hall (1970) applied to silica during spring runoff in Plastic 1.

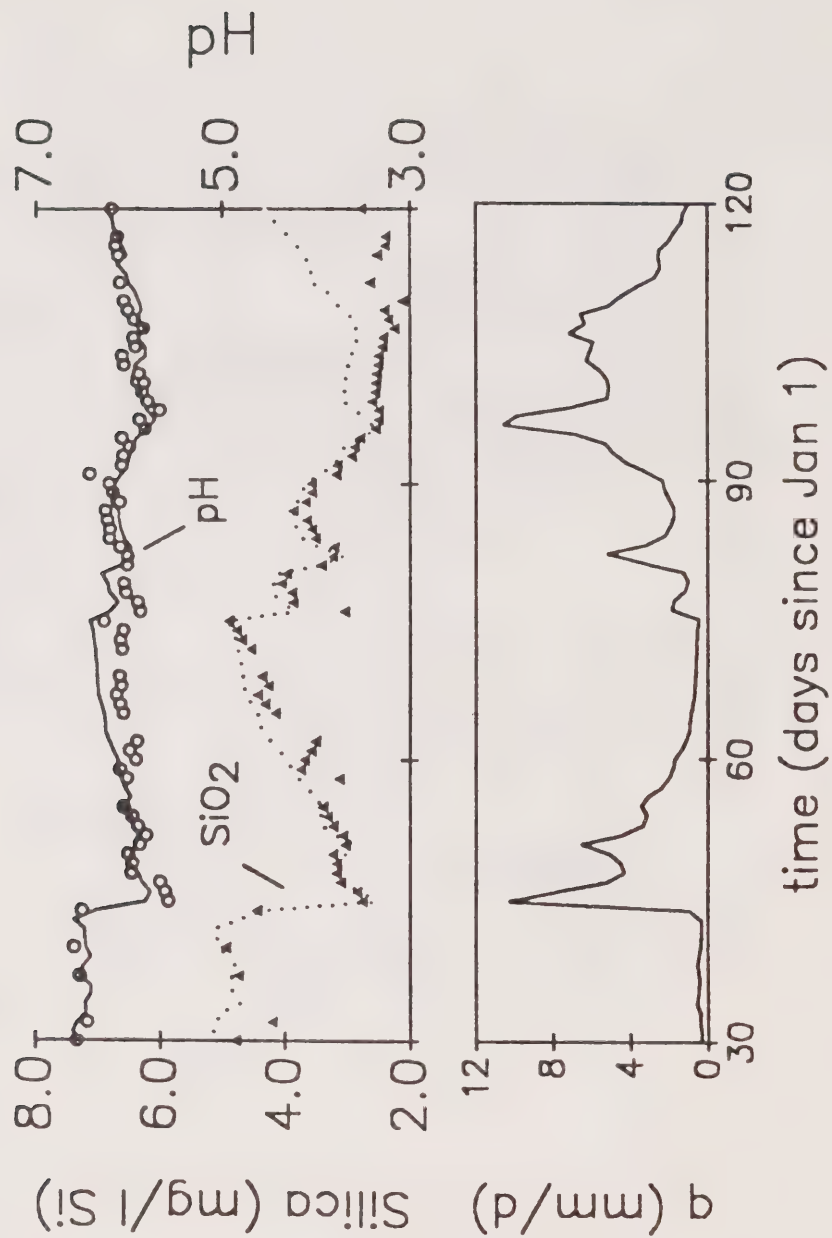


Fig. 7

Silica and pH simulation during spring runoff 1984 in Harp 4 based on the multiple regression model.

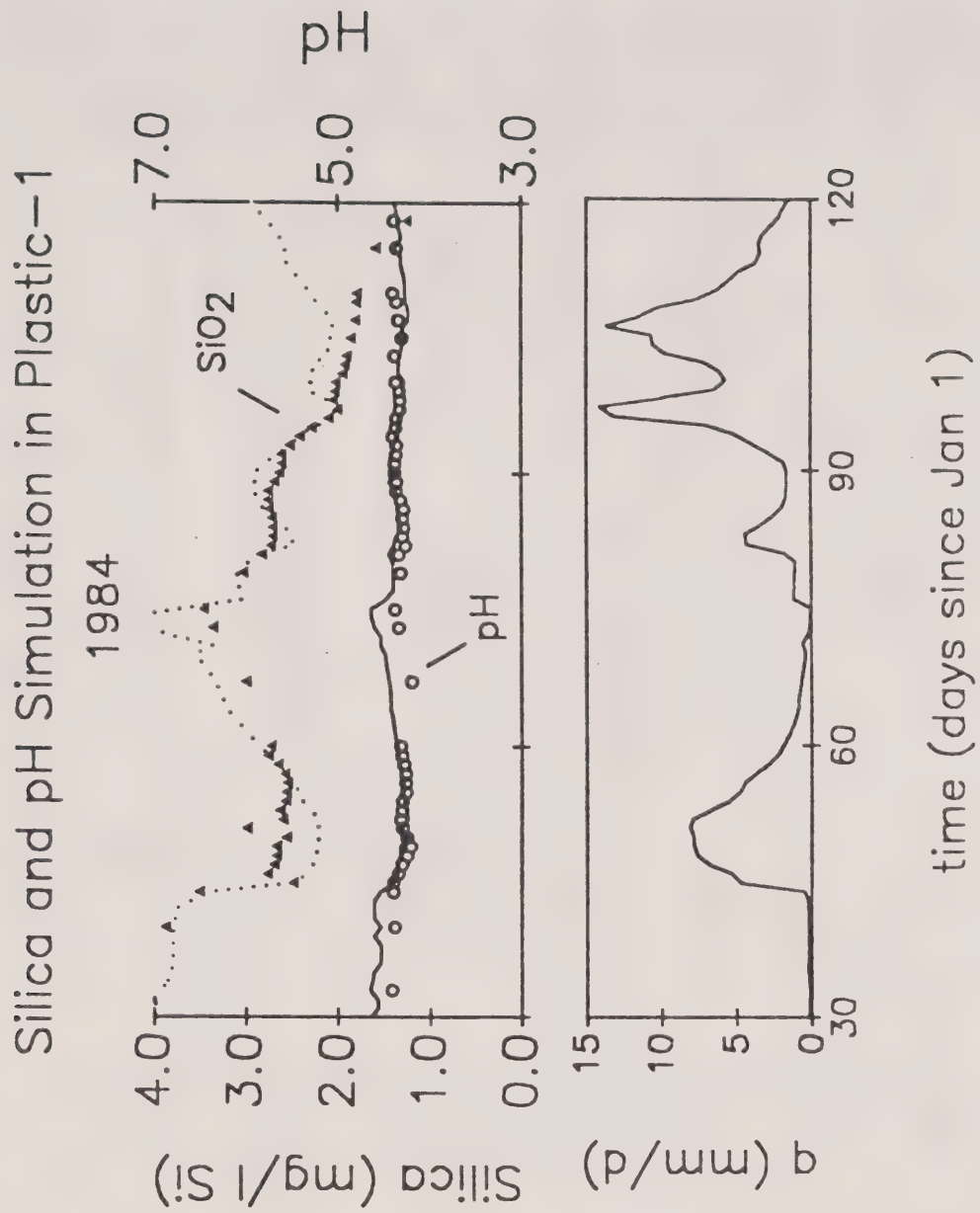


Fig. 8

Silica and pH simulation during spring runoff 1984 in Plastic 1 based on the multiple regression model.

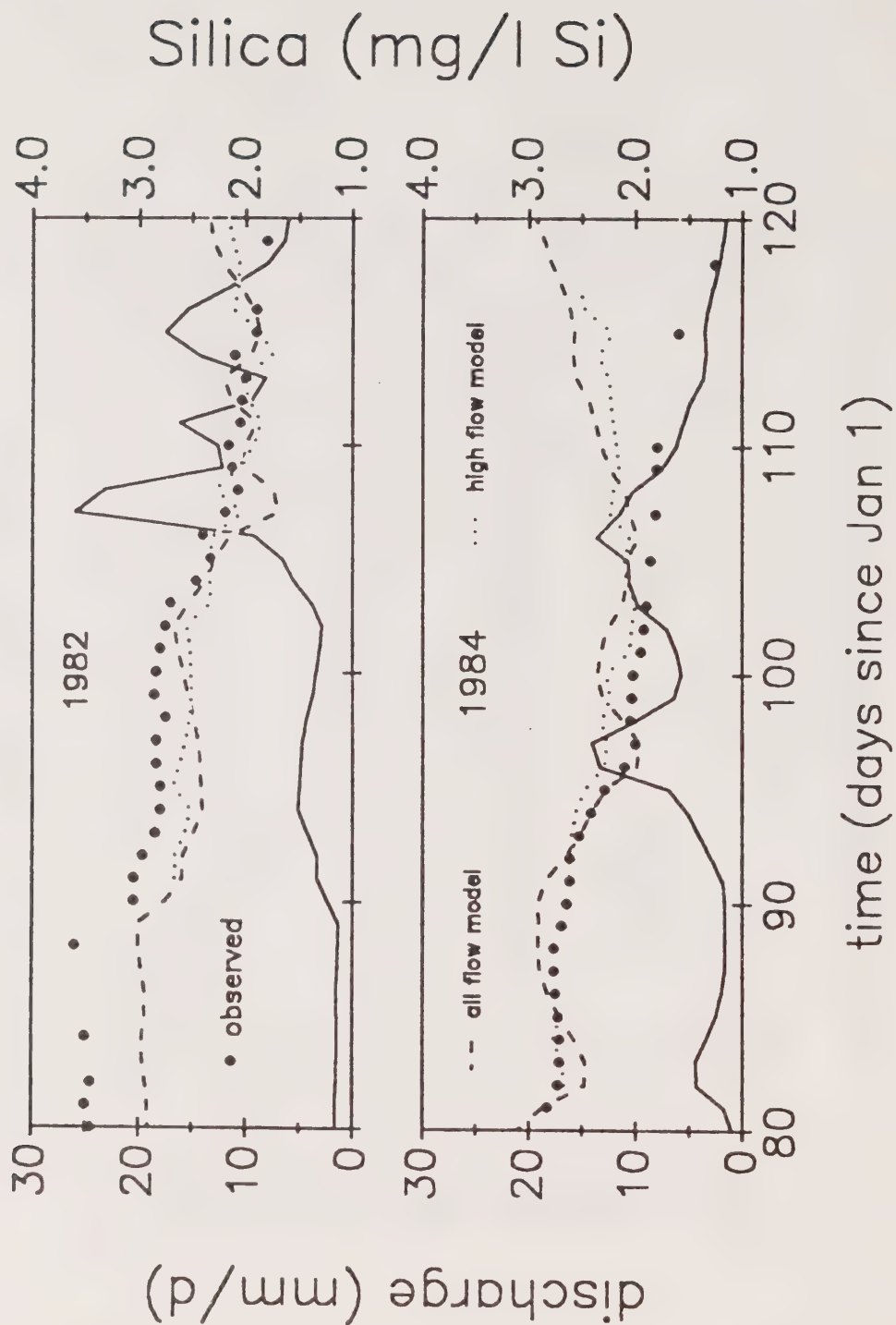


Fig. 9

Silica and pH simulation in Plastic 1 (1982 and 1984) based on the 'all flow' and 'high flow' model.

APPENDIX 1

Table 1. Correlation matrix for independent variables of flow selected for possible use in multiple regression analysis on stream solute behaviour . R-square values of correlation of each pair are given in %. Top values are calculated for Harp-4, bottom values for Plastic 1.

a) 'All flow' analysis

	X1	X2	X3	X4	X5
X1	/				
X2	70.7 80.2	/			
X3	34.6 24.4	16.5 15.8	/		
X4	3.0 0.6	0.9 2.1	26.1 13.6	/	
X5	6.7 1.5	0.1 2.0	3.2 0.3	3.2 3.9	/

b) 'High flow' analysis

	X1	X2	X3	X4	X5
X1	/				
X2	23.3 20.1	/			
X3	31.1 26.1	1.4 3.4	/		
X4	2.4 0.0	16.0 16.7	28.7 15.4	/	
X5	0.0 3.8	6.3 16.7	0.2 0.0	1.8 2.1	/

APPENDIX 2

Table II. Summary of regression models for stream solute behaviour using various flow variables (top values for Harp 4, bottom values for Plastic 1).

a) All flow analysis

$$[\text{Mg}^{2+}] = - 0.26 \log X1 + 1.03$$

[Mg²⁺] = not significant

$$[\text{SiO}_2] = - 1.73 \log X1 + 4.30$$

$$[\text{SiO}_2] = - 1.01 \log X1 + 3.12$$

$$[\text{H}^+] = 1.04 \log X1 + 0.09 X3 - 0.26 X5 + 0.66$$

$$[\text{H}^+] = 13.2 \log X1 - 0.85 X3 - 5.87 X5 + 40.2$$

b) High flow analysis

$$[\text{Mg}^{2+}] = - 0.30 \log X1 + 1.07$$

[Mg²⁺] = not significant

$$[\text{SiO}_2] = - 1.50 \log X1 + 4.12$$

$$[\text{SiO}_2] = - 0.87 \log X2 - 0.14 X4 - 0.21 X5 + 3.97$$

$$[\text{H}^+] = 1.69 \log X1 + 1.41 \log X2 + 0.20 X4 - 2.35$$

$$[\text{H}^+] = -0.41 X5 + 47.9$$

Table III. Correlation matrix for independent variables of storm parameters selected for possible use in multiple regression analysis on stream solute behaviour during storm events. R-square values of correlation of each pair are given in %.

in PLASTIC 1

	X1	X2	X3	X4	X5	X6
X1	/					
X2	23.0	/				
X3	59.5	29.3	/			
X4	1.7	28.6	9.8	/		
X5	61.4	11.0	60.1	11.6	/	
X6	10.5	2.4	2.0	13.5	10.6	/

APPENDIX 3

Table IV. Summary of hydrological storm characteristics recorded from mean daily discharge records of 14 selected storm events.

storm code	Qp (mm/d)	Qmax (mm/d)	Q range (mm)	# days from Qp to Qmax	day of peakflow
80/1	0.45	8.36	7.91	4	03/23/80
81/1	1.76	15.73	13.97	6	02/24/81
81/2	1.30	29.23	27.94	5	03/31/81
82/1	1.29	5.11	3.81	6	04/04/82
82/2	2.81	25.94	23.13	6	04/17/82
82/3	8.18	17.50	9.32	3	04/25/82
83/1	0.68	4.77	4.09	3	01/12/83
83/2	1.01	5.37	4.35	4	03/10/83
83/3	1.61	10.62	9.01	5	03/20/83
83/4	1.29	14.17	12.88	7	04/10/83
84/1	0.51	7.84	7.34	6	02/18/84
84/2	1.78	4.40	2.63	3	03/23/84
84/3	1.61	14.06	12.45	8	04/06/84
84/4	5.70	13.62	7.92	7	04/15/84

Qp : mean daily discharge recorded for last day before rise of storm hydrograph (prestorm discharge)

Qmax : mean daily discharge recorded for day of peak flow of storm hydrograph (maximum discharge)

Table V. Summary of independent storm variables of 14 selected storm events considered for multiple regression analysis.

storm code	X1 (mm)	X2 (mm)	X3 (mm/d)	X4 (mm)	X5 (deg.C)	X6 (days)
80/1	13.37	1.70	3.34	48.4	1.95	4
81/1	40.34	14.37	6.72	12.7	4.93	15
81/2	61.94	5.40	12.39	20.2	6.12	50
82/1	19.57	14.42	3.26	19.1	0.08	6
82/2	53.98	40.97	9.00	31.3	5.48	19
82/3	40.00	129.20	13.33	0.0	8.20	27
83/1	9.09	10.70	3.03	31.6	-5.73	3
83/2	13.32	2.56	3.33	6.2	3.45	60
83/3	28.03	31.54	5.61	13.1	2.86	70
83/4	40.51	7.93	5.79	28.8	4.06	101
84/1	32.88	2.48	5.48	38.2	3.42	6
84/2	10.51	7.70	3.50	10.7	0.77	40
84/3	35.45	24.93	4.43	15.6	2.59	54
84/4	63.64	69.84	9.09	14.9	5.31	63

APPENDIX 4

Table VI. Summary of dependent variables of 14 selected storm events considered for multiple regression analysis expressed as extreme values (A) and as range values (B) (deviation from prestorm []).

storm code	Extreme values		Range values	
	Group A		Group B	
	[H+] (ug/l)	[SiO ₂] (mg/l)	[H+] (ug/l)	[SiO ₂] (mg/l)
80/1	48.98	2.50	6.31	-2.60
81/1	45.71	2.35	35.48	-1.10
81/2	44.67	2.00	30.20	-1.40
82/1	45.71	2.80	38.02	-0.80
82/2	42.66	2.19	42.66	-0.56
82/3	44.67	1.90	44.67	-0.10
83/1	70.79	2.68	63.10	-0.07
83/2	45.71	2.75	30.90	-0.23
83/3	44.67	2.11	38.02	-0.35
83/4	41.69	1.77	35.48	-0.47
84/1	61.66	2.67	39.81	-0.84
84/2	50.12	2.71	45.71	-0.12
84/3	47.86	2.00	41.69	-0.64
84/4	45.71	1.81	42.66	-0.21

Table VII. Summary of regression models for storm solute behaviour.

a) Extreme values - Group A

$$[\text{SiO}_2] \text{ min} = - 0.86 \log X_1 - 0.005 X_6 + 3.73$$

$$[\text{H}^+] \text{ max} = - 1.74 X_5 + 54.03$$

b) Range values - Group B

$$[\text{SiO}_2] \text{ dev} = - 0.03 X_4 - 0.026$$

$$[\text{H}^+] \text{ dev} = \text{not significant}$$

